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## Use of statistical copolymers

The invention relates to the use of statistical copolymers as emulsifiers, in particular in the synthesis of nanoparticles, and to processes for the production of such particles.

The incorporation of inorganic nanoparticles into a polymer matrix can influence not only the mechanical properties, such as, for example, impact strength, of the matrix, but also modifies its optical properties, such as, for example, wavelength-dependent transmission, colour (absorption spectrum) and refractive index. In mixtures for optical applications, the particle size plays an important role since the addition of a substance having a refractive index which differs from the refractive index of the matrix inevitably results in light scattering and ultimately in light opacity. The drop in the intensity of radiation of a defined wavelength on passing through a mixture shows a high dependence on the diameter of the inorganic particles.

The development of suitable nanomaterials for dispersion in polymers requires not only control of the particle size, but also of the surface properties of the particles. Simple mixing (for example by extrusion) of hydrophilic particles with a hydrophobic polymer matrix results in inhomogeneous distribution of the particles throughout the polymer and additionally in aggregation thereof. For homogeneous incorporation of inorganic particles into polymers, their surface must therefore be at least hydrophobically modified. In addition, the nanoparticulate materials, in particular, exhibit a great tendency to form agglomerates, which also survive subsequent surface treatment.

Surprisingly, it has now been found that nanoparticles can be precipitated from emulsions directly with a suitable surface modification with

virtually no agglomerates if certain statistical copolymers are employed as emulsifier.

The present invention therefore relates firstly to the use of statistical copolymers containing at least one structural unit containing hydrophobic radicals and at least one structural unit containing hydrophilic radicals as emulsifier, in particular in the synthesis of nanoparticles from emulsions.

The present invention furthermore relates to a process for the production of polymer-modified nanoparticles which is characterised in that, in a step a), an inverse emulsion comprising one or more water-soluble precursors of the nanoparticles or a melt is prepared with the aid statistical copolymer of at least one monomer containing hydrophobic radicals and at least one monomer containing hydrophilic radicals, and, in a step b), particles are produced.

The emulsion technique for the production of nanoparticles is known in principle. Thus, M. P. Pileni; J. Phys. Chem. 1993, 97, 6961-6973, describes the production of semiconductor particles, such as CdSe, CdTe and ZnS, in inverse emulsions.

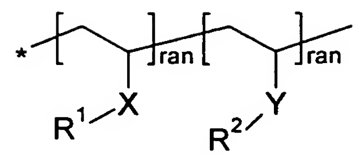
However, the syntheses of the inorganic materials frequently require high salt concentrations of precursor materials in the emulsion, while the concentration additionally varies during the reaction. Low-molecular-weight surfactants react to such high salt concentrations, and consequently the stability of the emulsions is at risk (Paul Kent and Brian R. Saunders; Journal of Colloid and Interface Science 242, 437-442 (2001)). In particular, the particle sizes can only be controlled to a limited extent (M.-H. Lee, C. Y. Tai, C. H. Lu, Korean J. Chem. Eng. 16, 1999, 818-822).

K. Landfester (Adv. Mater. 2001, 13, No. 10, 765-768) proposes the use of high-molecular-weight surfactants (PEO-PS block copolymers) in combination with ultrasound for the production of nanoparticles in the particle size range from about 150 to about 300 nm from metal salts.

The choice of statistical copolymers of at least one monomer containing hydrophobic radicals and at least one monomer containing hydrophilic radicals has now enabled the provision of emulsifiers which facilitate the production of inorganic nanoparticles from inverse emulsions with control of the particle size and particle-size distribution. At the same time, the use of these novel emulsifiers enables the nanoparticles to be isolated from the dispersions with virtually no agglomerates since the individual particles form directly with polymer coatings.
In addition, the nanoparticles obtainable by this method can be dispersed particularly simply and uniformly in polymers, with, in particular, it being possible substantially to avoid undesired impairment of the transparency of such polymers in visible light.

The statistical copolymers preferably to be employed in accordance with the invention exhibit a weight ratio of structural units containing hydrophobic radicals to structural units containing hydrophilic radicals in the statistical copolymers which is in the range from 1:2 to 500:1, preferably in the range from 1:1 to 100:1 and particularly preferably in the range from 7:3 to 10:1. The weight average molecular weight of the statistical copolymers is usually in the range from $M_w$ = 1000 to 1,000,000 g/mol, preferably in the range from 1500 to 100.000 g/mol and particularly preferably in the range from 2000 to 40.000 g/mol.

It has been found here that, in particular, copolymers which conform to the formula I



I

where

X and Y correspond to the radicals of conventional nonionic or ionic monomers, and

$R^1$ stands for hydrogen or a hydrophobic side group, preferably selected from branched or unbranched alkyl radicals having at least 4 carbon atoms, in which one or more, preferably all, H atoms may have been replaced by fluorine atoms, and

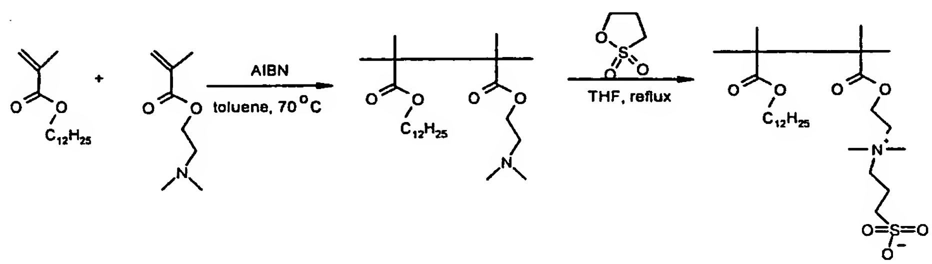
$R^2$ stands for a hydrophilic side group, which preferably has a phosphonate, sulfonate, polyol or polyether radical,

and where $-X-R^1$ and $-Y-R^2$ may each have a plurality of different meanings within a molecule that satisfy the requirements according to the invention in a particular manner.

Particular preference is given in accordance with the invention to polymers in which $-Y-R^2$ stands for a betaine structure.

Particular preference is in turn given here to polymers of the formula I in which X and Y, independently of one another, stand for -O-, -C(=O)-O-, -C(=O)-NH-, $-(CH_2)_n-$, phenyl, naphthyl or pyridyl. Furthermore, polymers in which at least one structural unit contains at least one quaternary nitrogen atom, where $R^2$ preferably stands for a $-(CH_2)_m-(N^+(CH_3)_2)-(CH_2)_n-SO_3^-$ side group or a $-(CH_2)_m-(N^+(CH_3)_2)-(CH_2)_n-PO_3^{2-}$ side group, where m stands for an integer from the range from 1 to 30, preferably from the range from 1 to 6, particularly preferably 2, and n stands for an integer from the range from 1 to 30, preferably from the range from 1 to 8, particularly preferably 3, can advantageously be employed.

Statistical copolymers particularly preferably to be employed can be prepared in accordance with the following scheme:




The desired amounts of lauryl methacrylate (LMA) and dimethyl-aminoethyl methacrylate (DMAEMA) are copolymerised here by known processes, preferably by means of free radicals in toluene through addition of AIBN. A betaine structure is subsequently obtained by known methods by reaction of the amine with 1,3-propane sultone.

Alternative copolymers preferably to be employed can contain styrene, vinylpyrrolidone, vinylpyridine, halogenated styrene or methoxystyrene, where these examples do not represent a limitation. In another, likewise preferred embodiment of the present invention, use is made of polymers which are characterised in that at least one structural unit is an oligomer or polymer, preferably a macromonomer, where polyethers, polyolefins and polyacrylates are particularly preferred as macromonomers.

Precursors which can be employed for the inorganic nanoparticles are water-soluble metal compounds, preferably silicon, cerium, cobalt, chromium, nickel, zinc, titanium, iron, yttrium and/or zirconium compounds, where these precursors are preferably reacted with an acid or lye for the production of corresponding metal-oxide particles.

Mixed oxides can be obtained in a simple manner here by suitable mixing of the corresponding precursors. The choice of suitable precursors presents the person skilled in the art with no difficulties; suitable compounds are all those which are suitable for the precipitation of the corresponding target compounds from aqueous solution. An overview of suitable precursors for the preparation of oxides is given, for example, in Table 6 in K. Osseo-Asare "Microemulsion-mediated Synthesis of nanosize Oxide Materials" in: Kumar P., Mittal KL, (editors), Handbook of microemulsion science and technology, New York: Marcel Dekker, Inc., pp. 559-573, the contents of which expressly belong to the disclosure content of the present application.

Hydrophilic melts can likewise serve as precursors of nanoparticles in the sense of this invention. A chemical reaction for the production of the nanoparticles is not absolutely necessary in this case.

In particular, alkali or alkaline earth metal silicates, preferably sodium silicates, as precursors can also be reacted with acid or lye to give silicon dioxide.

In likewise preferred embodiments of the present invention, at least one soluble compound of a noble metal, preferably silver nitrate, is reacted with a reducing agent, preferably citric acid, to give the metal.

For the preparation of nanoparticulate metal sulfides, which is likewise preferred in accordance with the invention, a soluble metal compound, preferably a soluble Pb, Cd or Zn compound, is reacted with hydrogen sulfide to give the metal sulfide.

In another embodiment of the present invention, a soluble metal compound, such as, preferably, for example, calcium chloride, is

reacted with carbon dioxide to give a nanoparticulate metal carbonate.

Nanoparticles particularly preferably produced are those which essentially consist of oxides or hydroxides of silicon, cerium, cobalt, chromium, nickel, zinc, titanium, iron, yttrium and/or zirconium.

The particles preferably have a mean particle size, determined by means of dynamic light scattering or a transmission electron microscope, of from 3 to 200 nm, in particular from 20 to 80 nm and very particularly preferably from 30 to 50 nm. In specific, likewise preferred embodiments of the present invention, the distribution of the particle sizes is narrow, i.e. the variation latitude is less than 100% of the mean, particularly preferably a maximum of 50% of the mean.

In the context of the use of these nanoparticles for UV protection in polymers, it is particularly preferred if the nanoparticles have an absorption maximum in the range 300 - 500 nm, preferably in the range up to 400 nm, where particularly preferred nanoparticles absorb radiation, in particular, in the UV-A region.

The emulsion process can be carried out here in various ways:
As already stated, particles are usually produced in step b) by reaction of the precursors or by cooling of the melt. The precursors can be reacted here, depending on the process variant selected, with an acid, a lye, a reducing agent or an oxidant.

For the production of particles in the desired particle-size range, it is particularly advantageous if the droplet size in the emulsion is in the range from 5 to 500 nm, preferably in the range from 10 to 200 nm. The droplet size in the given system is set here in the manner known

to the person skilled in the art, where the oil phase is matched individually to the reaction system by the person skilled in the art. For the production of ZnO particles, toluene and cyclohexane, for example, have proven successful as the oil phase.

In certain cases, it may be helpful to employ a further coemulsifier, preferably a nonionic surfactant, in addition to the statistical copolymer. Preferred coemulsifiers are optionally ethoxylated or propoxylated, relatively long-chain alkanols or alkylphenols having various degrees of ethoxylation or propoxylation (for example adducts with from 0 to 50 mol of alkylene oxide).

It may also be advantageous to employ dispersion aids, preferably water-soluble, high-molecular-weight, organic compounds containing polar groups, such as polyvinylpyrrolidone, copolymers of vinyl propionate or acetate and vinylpyrrolidone, partially saponified copolymers of an acrylate and acrylonitrile, polyvinyl alcohols having various residual acetate contents, cellulose ethers, gelatine, block copolymers, modified starch, low-molecular-weight, carboxyl- and/or sulfonyl-containing polymers, or mixtures of these substances.

Particularly preferred protective colloids are polyvinyl alcohols having a residual acetate content of below 40 mol%, in particular from 5 to 39 mol%, and/or vinylpyrrolidone-vinyl propionate copolymers having a vinyl ester content of below 35% by weight, in particular from 5 to 30% by weight.

The desired property combinations of the nanoparticles required can be set in a targeted manner by adjustment of the reaction conditions, such as temperature, pressure and reaction duration. The corresponding setting of these parameters presents the person skilled in the art with absolutely no difficulties. For example, work can be car-

ried out at atmospheric pressure and room temperature for many purposes.

In a preferred process variant, a second emulsion in which a reactant for the precursors is in emulsified form is mixed in step b) with the precursor emulsion from step a). This two-emulsion process allows the production of particles having a particularly narrow particle-size distribution. It may be particularly advantageous here for the two emulsions to be mixed with one another by the action of ultrasound.

In another, likewise preferred process variant, the precursor emulsion is mixed in step b) with a precipitant which is soluble in the continuous phase of the emulsion. The precipitation is then carried out by diffusion of the precipitant into the precursor-containing micelles. For example, titanium dioxide particles can be obtained by diffusion of pyridine into titanyl chloride-containing micelles or silver particles can be obtained by diffusion of long-chain aldehydes into silver nitrate-containing micelles.

The nanoparticles according to the invention are used, in particular, in polymers. Polymers into which the nanoparticles according to the invention can be incorporated well are, in particular, polycarbonate (PC), polyethylene terephthalate (PETP), polyimide (PI), polystyrene (PS), polymethyl methacrylate (PMMA) or copolymers comprising at least a fraction of one of the said polymers.

The incorporation can be carried out here by conventional methods for the preparation of polymer compositions. For example, the polymer material can be mixed with nanoparticles according to the invention, preferably in an extruder or compounder.
Depending on the polymer used, it is also possible to employ compounders.

A particular advantage of the particles according to the invention consists in that only a low energy input compared with the prior art is necessary for homogeneous distribution of the particles in the polymer.
The polymers here can also be dispersions of polymers, such as, for example, paints. The incorporation can be carried out here by conventional mixing operations.

The polymer compositions according to the invention comprising the nanoparticles are furthermore also particularly suitable for the coating of surfaces. This enables the surface or the material lying beneath the coating to be protected, for example, against UV radiation.

The following examples are intended to explain the invention in greater detail without limiting it.

## Examples

### Example 1: Synthesis of the macrosurfactants

The first step comprises the synthesis of a statistical copolymer of dodecyl methacrylate (lauryl methacrylate; LMA) and dimethylaminoethyl methacrylate (DMAEMA). Control of the molecular weight can be achieved by addition of mercaptoethanol. The copolymer obtained in this way is modified by means of 1,3-propane sultone in order to supply saturated groups.

To this end, 7 g of LMA and DMAEMA, in an amount corresponding to Table 1 below, are initially introduced in 12 g of toluene and subjected to free-radical polymerisation under argon at 70°C after initiation of the reaction by addition of 0.033 g of AIBN in 1 ml of toluene. The chain growth can be controlled here by addition of 2-mercaptoethanol (see Table 1). The crude polymer is washed, freeze-dried and subsequently reacted with 1,3-propane sultone, as described in V. Butun, C. E. Bennett, M. Vamvakaki, A. B. Lowe, N. C. Billingham, S. P. Armes, J. Mater. Chem., 1997, 7(9), 1693-1695.

The characterisation of the resultant polymers is given in Table 1.

Table 1: Amounts of monomers employed and characterisation of the resultant polymers

| | DMAEMA [g] | DMAEMA in the polymer [mol%] | 1-Mercapto-ethanol [g] | $M_n$ [g/mol] | $M_w$ [g/mol] | Betaine groups [mol%] |
|---|---|---|---|---|---|---|
| E1 | 1.08 | 19 | 0.033 | 18000 | 31000 | 16 |
| E2 | 1.08 | 19 | 0.011 | 28000 | 51000 | 19 |
| E3 | 1.08 | 21 | 0.066 | 13000 | 21000 | 21 |
| E4 | 1.09 | 20 | --- | 59000 | 158000 | 14.6 |
| E5 | 0.48 | 10.7 | --- | 52000 | 162000 | 7.5 |

**Example 2: Precipitation of ZnO particles**

ZnO particles are precipitated by the following method:

1. Preparation of in each case an inverse emulsion of an aqueous solution of 0.4 g of $Zn(AcO)_2{*}2H_2O$ in 1.1 g of water (emulsion 1) and 0.15 g of NaOH in 1.35 g of water (emulsion 2) by means of ultrasound. Emulsion 1 and emulsion 2 each comprise 150 mg of a statistical copolymer E1 – E5 from Table 1.
2. Ultrasound treatment of the mixture of emulsion 1 and emulsion 2, followed by drying.
3. Purification of sodium acetate by washing the resultant solid with water.
4. Drying and redispersal of the powder functionalised on the surface by the emulsifier by stirring in toluene.

FT-IR spectroscopy and X-ray diffraction show the formation of ZnO. Furthermore, no reflections of sodium acetate are visible in the X-ray diagram.

Thus, Example 2 results in a product which consists of the synthesised macrosurfactant and zinc oxide particles.

| Copolymer | Diameter [nm] (light scattering) | Variance [nm] | Proportion of ZnO (wt-%) |
|---|---|---|---|
| E1 | 37 | 30 | 30.3 |
| E2 | 66 | 53 | 30.5 |
| E3 | 50 | 41 | 32 |

**Comparative Example 2a: Use of the emulsifier ABIL EM 90®**

The procedure as described in Example 2 with the commercially available emulsifier ABIL EM 90® (cetyl dimethicone copolyol, Goldschmidt) instead of the statistical copolymer from Example 1 does not result in a stable emulsion. The particles obtained exhibit diameters of between 500 and 4000 nm.

**Example 3: Precipitation of silicon dioxide**

The precipitation of $SiO_2$ particles is carried out by the following method:
1. Preparation of in each case an inverse emulsion of an aqueous solution of $Na_2SiO_3$ (emulsion 1) and $H_2SO_4$ (emulsion 2) by means of ultrasound (concentrations corresponding to Table 2).
2. Ultrasound treatment of the mixture of emulsion 1 and emulsion 2 followed by drying.
3. Purification by washing the resultant solid with water.
4. Drying and redispersal of the powder obtained.

FT-IR spectroscopy and X-ray diffraction show the formation of $SiO_2$ and the non-presence/absence of sodium silicate.

The step thus gives a product which consists of the synthesised macro-surfactant and silicon dioxide particles.

**Table 2: Composition of the emulsions and characterisation of the products**

| Experiment | Emulsion E1 | Emulsion E2 | Particle size of the nanoparticles [nm] | Standard deviation [nm] |
|---|---|---|---|---|
| 3a | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 1.25 g of water 1.25 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 2.2 g of water; 0.3 g of $H_2SO_4$ | 59 | 19 |
| 3b | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 1.25 g of water; 1.00 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 1.76 g of water; 0.24 g of $H_2SO_4$ | 40 | 15 |
| 3c | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 0.75 g of water; 0.75 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E4); 11.7 g of toluene; 1.32 g of water; 0.18 g of $H_2SO_4$ | 50 | 20 |
| 3d | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 0.75 g of water; 0.75 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 1.32 g of water; 0.18 g of $H_2SO_4$ | 43 | 15 |
| 3e | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 1.25 g of water; 1.25 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 2.2 g of water; 0.3 g of $H_2SO_4$ | 53 | 12 |

| | | | | |
|---|---|---|---|---|
| 3f | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 1.0 g of water; 1.0 g of $Na_2SiO_3$ | 0.15 g of polymer surfactant (E5); 11.7 g of toluene; 1.76 g of water; 0.24 g of $H_2SO_4$ | 93 | 30 |

**Example 4: Polymer composition**

A dispersion of the particles from Example 2-E1 in PMMA lacquer is prepared by mixing, applied to glass substrates and dried. The ZnO content after drying is 10% by weight. The films exhibit a virtually imperceptible haze. Measurements using a UV-VIS spectrometer confirm this impression. The sample exhibits the following absorption values, depending on the layer thickness (the percentage of incident light lost in transmission is shown).

| Layer thickness | UV-A (350 nm) | VIS (400 nm) |
|---|---|---|
| 1.2 µm | 35% | 4% |
| 1.6 µm | 40% | 5% |
| 2.2 µm | 45% | 7% |

Comparison:

(ZnO (extra pure, Merck) in PMMA lacquer as above)

| | | |
|---|---|---|
| 2 µm | 64% | 46% |